Design of a Hierarchical Ternary Hybrid for a Fiber-Shaped Asymmetric Supercapacitor with High Volumetric Energy Density

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Supporting Information

ABSTRACT: A novel fiber-shaped supercapacitor is created with high volumetric energy density by designing an asymmetric configuration and integrating multiple functional components for electrodes. More specifically, a ternary hybrid fiber is prepared as a positive electrode by growing MnO_2 nanosheets onto a conducting polymer-coated carbon nanotube fiber; an ordered microporous carbon/carbon nanotube hybrid fiber is made as a negative electrode; and the hybrid positive and negative fibers are assembled into a fiber-shaped asymmetric supercapacitor. It shows a high operating voltage of 1.8 V, compared with 0.8–1.0 V of their conventional counterparts based on aqueous gel electrolytes; in particular, it produces an energy density as high as 11.3 mWh/cm³ which is on par with the thin-film lithium-ion batteries. It also exhibits remarkable cyclic stability and good rate performance. Due to the unique fiber shape, it can be woven or knitted into flexible power textiles.

1. INTRODUCTION

Tremendous attention has been paid to increase the energy density of a flexible supercapacitor to approach the levels of lithium-ion batteries without sacrificing their high power densities.^{1,2} A typical strategy is to extend the categories of the electrode materials.^{3,4} Up to date, diversified materials are explored as active materials in supercapacitors. For example, pseudocapacitive transition metal oxides/hydroxides are demonstrated to provide high specific capacitances and energy densities through redox reactions at their surfaces. Among them, MnO₂ is considered as the most promising electrode material because of the high theoretical specific capacitance (1380 F g^{-1}) ,⁵ wide potential window (0-0.9 V),⁶ environmental benignity, and low cost. However, the inferior electrical conductivity⁷ and unsatisfactory cycling stability have restricted their practical applications. The chronic degradation during cycling originated from the structural vulnerability of MnO₂ nanomaterials, which was produced by volumetric variations under charging and discharging.⁸ Poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PE-DOT:PSS), as a conducting polymer, is appreciated for the configurational flexibility which alleviates the damages from volumetric variation and benefits the cyclic stability.9,10 However, the electrical conductivity of PEDOT:PSS is not high enough to be kinetically favorable.¹¹ Differently, carbon nanomaterials such as carbon nanotubes (CNTs) are widely investigated for high electrical conductivities but unable to deliver highly capacitive performances.^{12,13} Since individual materials are less able to achieve all the requirements, a rational integration of multiple components that combine merits and offset the handicaps may provide a general and effective strategy.

1 - Contraction

Apart from improving the specific capacitance of the electrode material, extending the voltage window makes an enormous contribution to the increase of energy density as well.¹⁴ The energy density (E) of supercapacitor can be calculated as $E = 1/2CV^2$, where C is the specific capacitance and V represents the operating voltage of the total device. Generally, supercapacitors employ water-contained electrolytes such as poly(vinyl alcohol) gel electrolyte that intrinsically limit the operating window below the decomposition voltage.^{15,16} As an alternative, organic electrolytes can afford higher voltage but introduce safety vulnerabilities.¹⁷ To this end, the design of an asymmetric configuration may give a promising method to elevate the voltage level. In other words, a battery-like Faradaic positive electrode was employed to ensure high energy density, and the capacitor-like negative electrode was applied to provide high power density. To make a high-performance asymmetric supercapacitor, electrode material possessing porous structure and high electrochemical active specific surface area is highly demanded, e.g., reduced graphene oxide for positive electrode and porous carbon for negative electrode.¹⁸⁻²

Herein, a novel type of fiber-shaped supercapacitor with high volumetric energy densities is created by designing the asymmetric configuration and integrating multiple functional components as electrodes. As a demonstration to this strategy, we prepared a ternary hybrid positive electrode by growing

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 $\rm MnO_2$ nanosheets onto the conducting polymer-coated CNT fiber and then assembled it with an ordered microporous carbon (OMC)/CNT hybrid negative electrode. These fiber-shaped asymmetric supercapacitors (FASs) can be charged to a high voltage of 1.8 V, compared to 0.8–1.0 V of their conventional counterparts based on aqueous gel electrolytes. They achieve high energy densities up to 11.3 mWh·cm⁻³, which is close to the level of the thin film lithium-ion batteries. They also exhibit high flexibility, reasonable cycling performance, and good rate performance. The fiber shape reveals special advantages for flexible and wearable applications; e.g., electronic clothes can be woven and knitted from fiber-shaped supercapacitor.^{23–25}

2. EXPERIMENTAL SECTION

2.1. Preparation of OMC/CNT Fiber. To prepare the OMC/CNT hybrid fiber, 50 mg of OMC particles was dispersed into 10 mL of Nafion (5%) under probe sonication at 200 W for 20 min to form a suspension. Ten layers of aligned CNT sheets with thickness of ~180 nm were stacked together to form a laminar structure, followed by painting the above OMC suspension and then rolling into a hybrid fiber. The mass load of OMC was about ~67.5 μ g·cm⁻¹ (~76.1 wt % in the hybrid fiber).

2.2. Preparation of MnO₂/PEDOT:PSS/CNT Fiber. The bare CNT fiber was prepared by rolling stacked ten layers of aligned CNT sheets by a rotating motor. The CNT fiber was repeatedly dipped into the commercially available PEDOT:PSS solution and then subjected to the annealing step at 120 °C for 2 h. Dimethyl sulfoxide (5 wt %) and Zonyl FS-300 (1 wt %) fluorosurfactant were added to the PEDOT:PSS (Clevios PH1000) to enhance the electrical conductivity and promote wetting onto the CNT surface. In the formed CNT/ PEDOT:PSS hybrid fiber, the mass load of PEDOT:PSS was ~44 μ g·cm⁻¹. After that, MnO₂ nanomaterials were grown onto the PEDOT:PSS-coated CNT fiber through an electrochemical deposition process at a potential of 0.92 V in $Mn(NO_3)_2$ (0.02 M) and NaNO₃ (0.1 M) aqueous solutions. In a three-electrode system, the as-fabricated PEDOT:PSS/CNT hybrid fiber, Pt wire, and Ag/AgCl were served as the working, counter, and reference electrodes, respectively.

2.3. Assembly of the FAS. The all-solid-state FAS was assembled by employing the $MnO_2/PEDOT:PSS/CNT$ fiber and OMC/CNT fiber as positive and negative electrodes, respectively, and the carboxymethyl cellulose sodium (CMC)/ Na_2SO_4 gel as electrolyte. The CMC/ Na_2SO_4 gel electrolyte was obtained through mixing 3 g of CMC and 6 g of Na_2SO_4 in deionized water (50 mL) and kept at 80 °C for 3 h under vigorous stirring. After that, both the $MnO_2/PEDOT:PSS/CNT$ and OMC/CNT electrodes were coated with CMC/ Na_2SO_4 solution which also served as the separator and then allowed to dry at room temperature. Two hybrid fiber electrodes were finally twisted together to fabricate the FAS.

3. RESULTS AND DISCUSSION

The FAS fabrication is schematically illustrated in Figure 1. The negative electrode was obtained by paving a thin layer of OMC suspension on an aligned CNT sheet with thickness of \sim 180 nm, followed by rolling into a fiber. The aligned CNT sheet was prepared from a spinnable CNT array, which had been synthesized by chemical vapor deposition.²⁶ The content of OMC particles in the hybrid fiber was controlled by varying the



Figure 1. Schematic illustration to the fabrication of fiber-shaped asymmetric supercapacitor (FAS).

OMC concentration. A weight percentage of ~76.1% was mainly discussed in following parts. For the positive electrode, the aligned CNT sheet was first rolled into a CNT fiber; then a conductive PEDOT:PSS layer was coated on it through repeated "dip and coating" processes; MnO₂ nanosheets were deposited onto the as-obtained PEDOT:PSS/CNT fiber via electrochemical deposition.²⁷ The positive and negative electrodes were coated with CMC/Na₂SO₄ gel electrolyte and dried at room temperature. The resulting positive and negative fiber electrodes were finally twisted together to fabricate the FAS.

The scanning electron microscopy (SEM) image (Figure 2a) reveals the resulting CNT fiber has a uniform diameter of ~43 μ m with a highly aligned structure (Figure 2b), which enables high mechanical strength of $10^2 - 10^3$ MPa and electrical conductivity of $10^2 - 10^3$ S/cm as well as a large surface area.²⁸ For the negative fiber electrode, the diameter of the CNT hybrid fiber remained uniform after coating of the OMC suspension, and the OMC particles were incorporated among aligned CNTs (Figure S1, Supporting Information). During the preparation of the positive fiber electrode, a conductive PEDOT:PSS polymer layer was uniformly coated on the CNT fiber (Figure 2c and 2d). The energy-dispersive X-ray spectrometry (EDS) mapping reveals the uniform distribution of characteristic sulfur elements (Figure 2e). Through an electrochemical deposition, MnO2 nanosheets were homogeneously and perpendicularly grown onto the PEDOT:PSScoated CNT fiber (Figures 2f and 2g), which made MnO₂ more available to the electrolyte for redox reactions. Meanwhile, MnO₂ nanosheets are beneficial for high rate capability at high current density because they can greatly decrease the transport path of both ions and electrons. EDS mapping also shows the uniform distribution of Mn in the ternary hybrid fiber (Figure 2h). The cross-sectional SEM image also demonstrated the triaxial structure of the hybrid fiber (Figure S2, Supporting Information). The hybrid fiber showed a tensile strength of 162 MPa (Figure S3, Supporting Information). The chemical composition of the ternary hybrid fiber was further verified by X-ray photoelectron spectroscopy (Figure S4, Supporting Information) and discussed in the Supporting Information.



Figure 2. (a) and (b) Bare CNT yarn at low and high magnifications, respectively. (c) and (d) PEDOT:PSS/CNT hybrid fiber at low and high magnifications, respectively. (e) EDS mapping image of the S element at (d). (f) and (g) $MnO_2/PEDOT:PSS/CNT$ hybrid fiber with flower-like MnO_2 nanostructures grown on the surface at low and high magnifications, respectively. (h) EDS mapping image of the Mn element at (g).



Figure 3. (a) Comparative CV curves of four different electrodes at the same scan rate of 25 mV·s⁻¹ measured in a three-electrode system in 1.0 M Na_2SO_4 electrolyte. (b) Charge–discharge curves of the four different electrodes collected at a current density of 0.2 A·cm⁻³. (c) Dependence of the specific volumetric capacitance on the current density. (d) Comparative cycling performances of MnO_2/CNT , PEDOT:PSS/MnO₂/CNT, and $MnO_2/PEDOT:PSS/CNT$ fiber electrodes at 10 A·cm⁻³.

The electrochemical property of the $MnO_2/PEDOT:PSS/CNT$ hybrid fiber was characterized by the galvanostatic charge–discharge profiles and cyclic voltammetry (CV) with a three-electrode system in Na_2SO_4 electrolyte. Neutral Na_2SO_4 solution was used as the electrolyte since MnO_2 was instable in an acidic medium. Figure 3a compares CV curves of PEDOT:PSS/CNT, MnO_2/CNT , and $MnO_2/PEDOT:PSS/$

CNT fibers at 25 mV·s⁻¹. Obviously, the $MnO_2/PEDOT:PSS/CNT$ fiber delivers the highest specific capacitance. The symmetrical quasi-rectangular shape with two weak and broad redox peaks indicates an ideal electrochemical double layer along with a pseudocapacitive behavior. The weak and broad redox peaks resulted from the Faradaic reaction of MnO_2 . Such a quasi-rectangular CV shape could be maintained at 100 mV·



Figure 4. (a) Comparative CV curves of OMC/CNT and $MnO_2/PEDOT:PSS/CNT$ electrodes at 20 mV·s⁻¹. (b) Comparative charge–discharge curves of $MnO_2/PEDOT:PSS/CNT$ positive and OMC/CNT negative electrodes at the same current of 0.1 mA. (c) CV curves measured at different operating voltages at a constant scan rate of 20 mV·s⁻¹. (d) Charge–discharge curves collected at 0.26 A·cm⁻³ at the operating voltages ranging from 0.8 to 1.8 V.

s⁻¹ (Figure S5a, Supporting Information). The highest electrochemical property of the $MnO_2/PEDOT:PSS/CNT$ hybrid fiber electrode was verified by the prolonged discharge time (Figure 3b). The symmetrical triangular profile also indicates a desired capacitive behavior. The charge–discharge profiles further maintained the nearly symmetric feature, while the current density increased from 0.2 to 5 A·cm⁻³ (Figure S5b, Supporting Information).

In order to investigate the function of each component in the ternary hybrid electrode, the electrochemical characterizations of PEDOT:PSS/CNT, MnO₂/CNT, and MnO₂/PEDOT:PSS/ CNT are provided in Figures S6–8 (Supporting Information). For the PEDOT:PSS/CNT hybrid fiber, an almost rectangular CV shape was well maintained even at a scan rate as high as 500 mV·s⁻¹, demonstrating a high rate capability. The specific capacitances were slightly decreased from 61.2 F·cm⁻³ at 0.2 A· cm⁻³ to 50.4 F·cm⁻³ at 5 A·cm⁻³. For the MnO₂/CNT fiber, the electrochemical performance was improved significantly. The rectangular shape of the CV curves with two broad redox peaks at scan rates from 10 to 50 mV·s⁻¹ and symmetric triangular charge-discharge profiles at increasing current densities indicate its good capacitive behavior. The further wrapping of the CNT/MnO₂ fiber with a PEDOT:PSS layer sacrificed the specific capacitances revealed by the shrunken CV area and discharge time. The outermost polymer layer, to some extent, decreased the contact of the middle MnO2 with electrolyte.

The specific volumetric capacitances of the MnO₂/CNT, PEDOT:PSS/MnO₂/CNT, and MnO₂/PEDOT:PSS/CNT electrodes are calculated from their charge–discharge profiles and summarized in Figure 3c. The MnO₂/PEDOT:PSS/CNT electrode delivered very high specific capacitances of 478.6 F· cm⁻³ (or 411.6 F·g⁻¹) at 0.05 A·cm⁻³ and 267.3 F·cm⁻³ at 10 A·cm⁻³, which are higher than those of MnO₂/CNT (386.9 F· cm⁻³ at 0.05 A·cm⁻³ at 10 A·cm⁻³) and

PEDOT:PSS/MnO2/CNT (263 F·cm-3 at 0.05 A·cm-3 and 75.4 $F \cdot cm^{-3}$ at 10 $A \cdot cm^{-3}$) electrodes. The optimized mass load of MnO₂ in the MnO₂/PEDOT:PSS/CNT ternary hybrid fiber occurred at ~67% (Figure S9, Supporting Information), and too much load could increase the resistance and block the charge transportation. The PEDOT:PSS layer contributes to the good cycling performance. For example, the capacitance of MnO₂/PEDOT:PSS/CNT electrode exhibited a retention of as high as ca. 91% over 10 000 cycles, similar to the PEDOT:PSS/ MnO_2/CNT electrode. In contrast, only ~59% of the initial capacitance was maintained in the MnO₂/CNT electrode. For the MnO₂/PEDOT:PSS/CNT electrode, the middle PE-DOT:PSS layer with polymeric flexibility might serve as a binder material for anchoring the outer MnO₂ nanosheets to prevent them from detaching from the smooth CNT fiber surface during repeated charge-discharge cycling. Meanwhile, the conducting polymer also introduces pseudocapacitance based on redox reaction, which contributes to more charge storage.

The electrochemical performances of the OMC/CNT hybrid fiber were also investigated in 1 M Na₂SO₄ electrolyte with a three-electrode system. When the scan rates were increased from 10 to 200 mV·s⁻¹, a rectangular shaped CV curve is well maintained (Figure S10a, Supporting Information), indicating a good electrochemical double-layer behavior of the OMC/CNT electrode. The charge–discharge profiles measured at various current densities share a symmetrical triangle shape in the voltage window within -1-0 V (Figure S10b, Supporting Information). It delivers a specific volumetric capacitance of 121.4 F·cm⁻³ (or 116.3 F·g⁻¹) at 0.43 A·cm⁻³ and remains at 101.9 F·cm⁻³ at a current density as high as 3.44 A·cm⁻³.

The $MnO_2/PEDOT:PSS/CNT$ hybrid positive electrode and OMC/CNT hybrid negative electrode were carefully matched and optimized to maximize the voltage window and specific capacitance of the proposed FAS. Figure 4a compares



Figure 5. (a) CV curves of the FAS measured at increasing scan rates from 0 to 1.8 V. (b) Charge and discharge curves collected at increasing current densities. (c) Specific volumetric capacitances calculated based on the whole device. (d) Ragone plots of our FASs compared with the commercially available energy storage devices^{21,30-32} and previous FASs.^{33,34} Here AC and SC represent activated carbon and supercapacitor, respectively.

the CV curves of the MnO₂/PEDOT:PSS/CNT positive electrode and OMC/CNT negative electrode at 20 mV s⁻¹. The positive and negative electrodes reveal stable operating voltages within 0-0.8 V and -1-0 V, respectively. Therefore, we anticipate that the maximal operating voltage of the proposed FAS can achieve 1.8 V. For an asymmetrical supercapacitor, the charge (Q) stored by two electrodes should follow the two equations of $Q^+ = Q^-$ and $Q = C \times \Delta E$ to maximize the capacitance.²⁹ Here C stands for the volumetric capacitance of two electrodes, and ΔE represents the potential window for the charge/discharge process of positive or negative electrode. As the two fiber electrodes are lightweight, the volumetric capacitance is chosen to substitute the commonly used gravimetric capacitance. As the value of $\Delta E^+/\Delta E^-$ is 0.8 in this study, the optimal volumetric capacitance ratio of the two electrodes (C^+/C^-) should be 1.25. Figure 4b compares charge-discharge curves of the MnO2/PEDOT:PSS/CNT positive electrode and the OMC/CNT negative electrode. At charging current of 0.1 mA, the volumetric capacitances of the two electrodes obey the relation of $C^+/C^- = 1.25$, as revealed by their similar discharge time.

As expected, the as-fabricated FAS shows highly stable electrochemical performances in different voltage windows. For example, the CV profiles collected at 20 mV·s⁻¹ remain rectangular even as the voltage window expanded to 1.8 V (Figure 4c). Figure 4d gives the charge–discharge profiles in different ranges of voltage at 0.26 A·cm⁻³. The charge and discharge profiles at each voltage reveal a symmetrical relationship up to 1.8 V, and the times for discharge are nearly linear variation with the cell voltage. With the extending voltage windows from 0.8 to 1.8 V, the calculated specific capacitances of the whole device (including electrolyte and two fiber-shaped electrodes) slightly increased from 13.4 to 19.1 F·cm⁻³. Accordingly, the energy density of the FAS is improved by 517% (from 1.2, 2.2, 3.4, 4.7, and 6.3 to 8.6 mWh \cdot cm⁻³) with the increasing operating voltages.

The as-fabricated FAS exhibited an ideal capacitive behavior in the whole voltage window within 0-1.8 V. For instance, the CV profiles share a rectangular shape at 200 mV·s⁻¹ (Figure 5a). The high electrochemical performances of the FASs are also confirmed by the symmetrically triangular shape of the charge and discharge profiles measured at various current densities (Figure 5b). Calculated from the charge-discharge profiles, the specific volumetric capacitances of the whole FAS device are summarized in Figure 5c. It achieved a high capacitance of 23.4 $\text{F} \cdot \text{cm}^{-3}$ (or 21.7 $\text{F} \cdot \text{g}^{-1}$) at 0.085 $\text{A} \cdot \text{cm}^{-3}$ and remained 13.3 F·cm⁻³ at higher current density of 2.38 A·cm⁻³ indicating a good rate capability. Compared with the MnO₂/ CNT, the lower equivalent series resistance for the MnO₂/ PEDOT:PSS/CNT was verified by electrochemical impedance spectrum (Figure S11, Supporting Information). The leakage current of the FAS was measured as 0.41 μ A after 5 h in air (Figure S12, Supporting Information). Figure S13 (Supporting Information) shows the self-discharge test of the FAS with 0.92 V being retained after resting for 2 h.

The high specific capacitance and operating voltage of the FAS promise a high energy density, while the sustainable high currents also enable the device with a high power density. For example, the FAS delivered a maximum volumetric energy density of 11.3 mWh·cm⁻³ (at power density of 0.03 W·cm⁻³) and volumetric power density of 2.1 W·cm⁻³ (at volumetric energy density of 6 mWh·cm⁻³). Figure 5d further compares the volumetric energy/power densities of this FAS with the commercially available energy storage devices and other FASs. The energy density in this work is more than ten times higher than those of the commercially available supercapacitors (2.75 V/44 mF, 5.5 V/100 mF)^{16,30} with volumetric energy densities less than 1 mWh·cm⁻³ and even on par with the thin-film lithium-ion battery (4 V/500 μ Ah) with the maximal energy

density of ~9 mWh·cm^{-3,31,32} The volumetric energy density value is also higher than the ever reported maximum values in MnO_2 -based FASs,^{33–36} such as the N-doped reduced graphene oxide (rGO)/CNT//rGO/CNT/MnO₂ FAS (5 mWh·cm⁻³)³³ and rGO/CNT//rGO/MnO₂ FAS (5.5 mWh·cm⁻³).³⁴ The remarkable performances of the obtained FAS could result from the following factors: (1) both the positive and negative electrodes can exhibit large volumetric capacitances that endow the assembled FAS with a high specific capacitance; (2) the FAS can be charged to a high voltage of 1.8 V; (3) additional current collectors, binders, separators, and some other packing materials are avoided, greatly reducing the volume of the whole device.

We further investigated the stability and flexibility of the fabricated FAS. The cycling stability was tested at 1.36 A·cm⁻³ with 85% capacitance retention over 10 000 charge-discharge cycles (Figure S14, Supporting Information). The flexibility of the FAS was investigated by tracing the capacitances under repeated bending cycles. The specific capacitances remained almost unchanged even after bend and release for 5000 times (Figure S15, Supporting Information), as revealed by the well overlapped charge-discharge curves collected at different bending cycles. Owing to the flexibility, several FASs can be integrated in series and parallel to achieve higher operating voltages and output currents, respectively. For example, the operating voltage was doubled and tripled from 1.8 V for single FAS by connecting two and three FASs in series, respectively (Figure S16a, Supporting Information). The shapes of the voltage profiles retained perfectly, indicating that the integrated devices were stably performed. The output currents were also doubled and tripled when connected to two and three FASs in parallel within 0–1.8 V, respectively (Figure S16b, Supporting Information). The output voltage/current after integration can be designed to meet various specific requirements which is significant for practical application.

4. CONCLUSION

In summary, a ternary hybrid electrode composed of MnO₂ nanosheets grown on conducting polymer-coated aligned CNT skeleton was carefully designed. It delivered an excellent specific volumetric capacitance and exhibited good rate performance as well as high cyclic stability. An aqueous FAS with a wide potential window of 0-1.8 V was further achieved by matching the ternary hybrid fiber as a positive electrode with OMC/CNT as the negative electrode. The FAS delivered a high volumetric energy density of $\sim 11.3 \text{ mWh} \cdot \text{cm}^{-3}$ that is superior to the other FASs and even on par with the 4 V/500 μ Ah thin-film lithium-ion battery. A high volumetric power density of $\sim 2.1 \text{ W} \cdot \text{cm}^{-3}$ is also analogous to the commercially available bulk supercapacitors. The high flexibility makes it feasible to connect them in series/parallel to enhance the energy/power outputs. This work opens a facile avenue to fabricate high-performance FASs with remarkable energy density and high operation voltage that are greatly required in a variety of applications.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b02794.

Experimental section, electrochemical parameters calculation, XPS analysis, cross-sectional SEM, stress-strain

curve, electrochemical characterizations of electrodes and devices, and flexibility and cycle performances of FASs (PDF)

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Notes

The authors declare no competing financial interest.

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