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Flexible All-Solid-State 2.4 V Aqueous Asymmetric Microsupercapacitors with Ultrahigh Energy Density

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Tremendous research efforts have recently been devoted to high-energy-density flexible all-solid-state microsupercapacitors (MSCs) to satisfy the rapidly increasing demand of wearable and portable electronics. However, both low operating voltage and unsatisfactory specific capacitance hinder their widespread applications in high-energy-consumption personal electronic devices. Here, we demonstrate a simple and cost-effective cut-and-transfer way to fabricate flexible all-solid-state 2.4 V aqueous asymmetric MSCs (AMSCs) by employing hierarchical Na-MnO_x nanosheets on 3D nitrogen-doped carbon fiber (Na-MnO_x@NCF) as the positive electrode and carbon-coated VN nanowire arrays (VN@C NWAs) as the negative electrode. Taking advantage of the high specific capacitance and wide electrochemical potential window of the electrode materials, the resulting AMSCs exhibit a large specific capacitance of 96.6 mF/cm² and a high energy density of 77.28 μWh/cm², outperforming most previously reported MSCs. Additionally, our device delivers negligible capacitance decay after bending 3,000 times, indicating its outstanding mechanical flexibility. Thus, this work provides a new way to develop high-voltage aqueous AMSC for the next-generation wearable energy-storage devices.

1. Introduction

Ever-increasing demand for portable and wearable electronics has stimulated considerable attention in quest for high-performance micro-sized energy storage devices. As a novel class of microscale electrochemical power source, microsupercapacitors (MSCs) with small size, controllable patterning, high power density, long cycle life and the capability of on-chip integration are particularly intriguing. Despite great advances have been achieved in MSCs by adopting lithographic and laser scribing microfabrication techniques, their energy density is yet unsatisfactory, which is caused by low operating voltage and small specific capacitance. To address these challenges, constructing asymmetric MSCs (AMSCs) is an effective approach to widen the voltage window and accordingly increase the energy density. Recently, great efforts have been made to develop high-performance AMSCs, but their operating voltage is typically lower than 2 V which cannot meet the power requirement of the high-energy-consumption personal electronic devices. Therefore, high-voltage (beyond 2V) AMSCs with ultrahigh power density are highly desirable for powering the next-generation wearable electronic devices.

In the past few years, huge research efforts were devoted to developing carbon-based MSCs using conventional microfabrication techniques. Compared with carbon-based nanomaterials that rely on electrochemical double layer capacitors to store energy, pseudocapacitive materials with reversible and rapid surface redox reactions show higher specific capacitance and energy density. Recently, cut-and-transfer technology has been used to pattern interdigitated 3D Ni foam current collectors as the frameworks for directly grown massive electroactive material, which provides a simple way to develop high-performance AMSCs. Carbon nanotube film (CNTF) has been considered the most promising candidates for high-performance electrodes because of its light weight, outstanding mechanical flexibility and high conductivity. Therefore, to synthesize wide-voltage positive and negative electrode materials on CNTF is a promising way to achieve high-energy-density flexible AMSCs.

Among the various positive electrode materials, manganese oxides offer high theoretical specific capacitance, wide electrochemical potential window, natural abundance and environmental benignity. Recent studies have shown that insertion Na^+ into MnO_x is a very effective way to extend its potential window. However, it remains a fundamental challenge to further improve the specific capacitance of Na doped MnO_x (Na- MnO_x). Herein, to address this challenge, we construct a three-dimensional (3D) conductive support for hosting sufficient Na- MnO_x . To be specific, we directly deposit Na- MnO_x nanosheets on 3D nitrogen-doped carbon fiber (Na- MnO_x @NCF) to form core-shell heterostructures as a novel binder-free electrode. Such an intriguing core-shell structure provides abundant electroactive sites and short electron and ion diffusion paths for rapid pseudocapacitive reaction. As a proof-of-concept demonstration, we successfully assemble AMSCs by adopting hierarchical Na- MnO_x @NC/CNTF as the positive electrode and carbon-coated VN nanowire arrays (VN@C NWAs) as the negative electrode, and a wide voltage window of 2.4 V is achieved, which is the highest voltage window reported so far in an AMSC. The electrochemical results show that our as-prepared AMSCs exhibit a remarkable specific capacitance of 96.6 mF/cm^2 and a high energy density of 77.28 $\mu\text{Wh}/\text{cm}^2$. In addition, our device exhibits superior mechanical stability that its capacitance has negligible decay after bending 3,000 times.

2. Results and discussion

Figure 1 illustrates the schematic fabrication process of the AMSC and the details are presented in the experimental section. The interdigitated CNTF was used as a current collector and flexible electrode for further loading electroactive materials. First, NCF nanowires were directly grown on interdigitated CNTF through a two-step process including the electropolymerization of polypyrrole nanowires (PPy NWs) and post carbonization treatment in argon. Thereafter, Na- MnO_x nanosheet was uniformly coated onto the surface of each NCF nanowire via an electrodeposition method to act as a positive electrode.

Meanwhile, VN@C NWAs were directly synthesized on CNTF according to our previous work for being used as a negative electrode [ref]. Finally, the AMSC was successfully assembled by attaching the Na-MnO_x@NC/CNTF and VN@C/CNTF on PDMS after coating them with a thin layer of Na₂SO₄/carboxymethyl cellulose sodium (CMC) gel electrolyte.

The scanning electron microscopy (SEM) images in Figure 2a and 2b clearly demonstrate that NCFs were uniformly grown on the surface of CNTF after electropolymerization of polypyrrole nanowires and subsequent high-temperature calcination. After the electrodeposition process, the MnO_x nanosheets were homogeneously anchored onto the surfaces of the as-fabricated NCF nanowires to form hierarchical core-shell structures and the following insertion Na⁺ process was carried out with the CV method between 0 and 1.3 V in a saturated Na₂SO₄ aqueous solution (Figure 2c). Furthermore, the low-resolution transmission electron microscopy (TEM) image (Figure 2d) reveals that Na-MnO_x nanosheets possess ultrathin feature. The X-ray photoelectron spectroscopy (XPS) pattern of the Na-MnO_x nanosheets (Figure 2e) contains only the major peaks of both MnO_x and Na⁺, indicating that the fabricated electroactive material consists solely of Mn, O and Na elements. The chemical compositions and valence states of the Na-MnO_x nanosheets were presented in Figure S1. The chemical compositions were further investigated with energy-dispersive spectroscopy (EDS), as shown in Figure 2f, again providing clear evidence of the coexistence of Mn, O, and Na elements. Moreover, the EDS mapping reveals the homogeneous distribution of Mn, O and Na on the whole nanosheet (Figure 2g).

The electrochemical properties of the as-prepared Na-MnO_x@NCF/CNTF positive electrode and VN@C NWAs/CNTF negative electrode are respectively examined in a three-electrode configuration using 1M Na₂SO₄ aqueous solution as the electrolyte, a platinum wire as the counter electrode and Ag/AgCl as the reference electrode. The typical CV curves of the Na-MnO_x@NCF/CNTF in different potential windows of 0-0.8, 0-1.0 and 0-1.2 V are shown in Figure 3a. It is noted that all CV curves display quasi-rectangular shapes, even at a high potential up to 1.2 V. Furthermore, the galvanostatic charge/discharge (GCD) curves of the Na-MnO_x@NCF/CNTF collected over different voltages from 0.8 to 1.2 V at a current density of 4 mA/cm², shown in Figure S2, clearly demonstrate that the voltage window of Na-MnO_x can reach 1.2 V. The CV curves of Na-MnO_x@NCF/CNTF were measured with a voltage window of 0-1.2 V at scan rates between 5 and 50 mV/s (Figure 3b). All the CV curves exhibit the ideal quasi-rectangular shapes without redox peaks, demonstrating the excellent reversibility of Na-MnO_x@NCF/CNTF. The linear and symmetric GCD curves of Na-MnO_x@NCF/CNTF in potential windows of 0-1.2 V at different current densities from 1-10 mA/cm² are plotted in Figure 3c, further confirming its excellent capacitance behavior. The areal specific capacitances of the prepared Na-MnO_x@NCF/CNTF, calculated from the GCD curves as a function of the current densities, are shown in Figure 3d. A high capacitance of 636.4 mF/cm² can be achieved at a current density of 1 mA/cm², and it still maintained 436.8 mF/cm² even at a high current density of 10 mA/cm², demonstrating an outstanding rate capability. To complement the Na-MnO_x@NC with wide voltage window, VN@C NWAs were successfully fabricated according to our previous report. As shown in Figure S3, the entire CNTF surface was uniformly covered by the VN NWAs. X-ray diffraction (XRD) is used to further investigate the structure of as-fabricated VN NWAs and the detailed information is shown in Figure S4. Figure 3e shows the typical CV curves of the VN@C NWAs/CNTF measured with a voltage window of -1.2 to -0.2 V at scan rates from 5 to 50 mV/s. All of the CV curves distorted from the rectangular shape, which confirm the pseudocapacitive behavior of the VN@C NWAs/CNTF. The discharge curves of the VN@C NWAs/CNTF at various current densities ranging from 4 to 10 mA/cm² are shown in Figure 3f. The near linear curves demonstrate its exceptional capacitive behavior and a high specific capacitance of 760.5 mF/cm² is achieved at the constant current density of 4 mA/cm².

To investigate the device's total voltage, we measured the CV curves of NV@C NWAs/CNTF and Na-MnO_x@NCF/CNTF electrodes in separate potential windows of -1.2-0.2 V and 0-1.2 V at a scan rate of 25 mV/s (Figure 4a). Based on the separate potential windows, the operating voltage for the assembled AMSC consisted of NV@C NWAs/CNTF as the negative electrode and Na-MnO_x@NCF/CNTF as the positive electrode reaches 2.4 V. Figure 4b shows the CV curves of the NV@C NWAs/CNTF// Na-MnO_x@NCF/CNTF device at a scan rate of 25 mV/s in different potential windows. The CV curves maintain the ideal rectangular shape even when the cell voltage increases to 2.4 V, indicating the excellent capacitive behavior and fast charge/discharge capability of our AMSC. This result is further confirmed by the nearly symmetric charge-discharge curves of the AMSC at an operating potential up to 2.4 V (Figure 4c). Figure 4d shows the areal specific capacitances and energy density (based on the areal of the entire device) of the assembled AMSC device calculated from the GCD curves collected at 6 mA/cm² as a function the potential window. Notably, both the areal specific capacitance and energy density of our AMSC significantly increase with the operating potential increasing from 1.2 to 2.4 V.

To further characterize the performance of the assembled AMSC device, the CV curves were measured at various scan rates in the potential window of 0-2.4 V. As shown in Figure 5a, the CV curves maintain the quasi-rectangular shape without apparent redox peaks even at a high scan rate of 200 mV/s. The nearly linear and symmetric GCD curves at various current densities, as demonstrated in Figure 5b, further prove the excellent pseudocapacitive properties and Faradaic reversibility of our assembled AMSC device. As presented in Figure 5c, a high capacitance of 96.8 mF/cm² is achieved at a current density of 1.5 mA/cm², and a capacitance of 77.1 mF/cm² can be maintained when the current density increases to 15 mA/cm², indicating an impressive rate capability. Energy density and power density are important parameters to evaluate the performance of the supercapacitors. An energy density of 77.28 μWh/cm² can be achieved at a power density of 1806.55 μW/cm², and the energy density 61.68 μWh/cm² is still even at a power density increased to 19650.27 μW/cm² (Figure 5d). These data considerably exceed the previously reported MASCs, including V₂O₅//MnO₂ (0.88 μWh/cm², 160 μW/cm²), graphene quantum dots//MnO₂ (0.414 μWh/cm², 15 μW/cm²), rGo-Ni//rGo-Ni (0.51 μWh/cm², 2400 μW/cm²), PPy//PPy (4 μWh/cm², 185 μW/cm²) and cellular graphene//cellular graphene (0.22 μWh/cm², 370 μW/cm²). The Nyquist plot of the as-assembled AMSC over the frequency range of 10⁻² to 10⁵ Hz is shown in Figure S5. The equivalent series resistance of our device was as low as 13.7 Ω and nearly 90° in the low frequency region indicates the ideal capacitive behavior. In addition, the capacitance retention of our MASC could reach 91.6% after long-term charging/discharging cycling at 2 mA/cm² for 5,000 cycles, as illustrated in Figure S6, demonstrating that our MASC has an superior cyclic ability. After charging to 2.4 V, the assembled AMSC device can light up a red light emitting diode (LED) as shown in Figure 5e. As illustrated in Figure 5f, it can be clearly seen that these CV curves of assembled MASC device almost overlap completely with different bending angles from 0° to 180°, highlighting its excellent mechanical stability. Furthermore, Figure S7 demonstrates negligible changes in the GCD curves at a current density of 3 mA/cm² after bending at 90° for more than 3,000 times, again confirming the exceptional flexibility of our MASC.

3. Conclusion

In summary, we successfully fabricated flexible all-solid-state 2.4 V AMSCs by employing hierarchical Na-MnO_x@NCF/CNTF as the positive electrode and VN@C NWAs/CNTF as the negative electrode with a facile cut-and-transfer method. As a result of the high specific capacitance and wide electrochemical potential window of the negative and the positive electrode materials, a high specific capacitance of 96.6 mF/cm² and an energy density of 77.28 μWh/cm² were achieved for our AMSC device, which are higher than most previously reported state-of-the-art MSCs. In addition, our device showed negligible

capacitance decay after bending 3,000 times, indicating its excellent mechanical stability. Thus, the proposed method constitutes a relatively simple and cost-effective strategy for the rational design and fabrication of prototype high-voltage AMSCs with superior electrochemical performance.

4. Experimental section

Preparation of Na-MnO_x@NCF/CNTF: The interdigitated CNTF was acquired via laser cutting technology. First, NCFs were synthesized by the electropolymerization of PPy NWs and post-carbonization procedure. The electropolymerization of polypyrrole nanowires was carried out with the similar method according to previously reported work [ref]. The as-prepared PPy NWs were annealed at 600 °C in argon for 2 h to obtain NCFs. Thereafter, MnO_x nanosheets were directly deposited on the NCF/CNTF in a mixed aqueous solution of 0.05 M MnSO₄, 0.05 M CH₃COONa, and 10% vol ethanol with a current density of 5mA/cm². The insertion Na⁺ process was carried out with the CV method between 0 and 1.3 V in saturated Na₂SO₄ solution with the scan rate of 15 mV/s for 500 cycles. After these procedures, the positive electrode came into being.

Assembly of VN@C NWAs/CNTF//Na-MnO_x@NCF/CNTF AMSCs: The as-fabricated AMSCs were assembled by adopting hierarchical Na-MnO_x@NCF/CNTF as the positive electrode, VN@C NWAs/CNTF as the negative electrode, and Na₂SO₄-CMC as gel electrolyte. The Na₂SO₄-CMC gel electrolyte was prepared by mixing 10 g Na₂SO₄ and 6 g PVA in 100 mL distilled water under vigorous stirring at 85°C for 2 h until the solution became clear. The prepared interdigitated VN@C NWAs/CNTF and VN@C NWAs/CNTF were attached to the side of thin PDMS film, followed by coating with a thin layer of Na₂SO₄-CMC gel electrolyte and maintaining at 60 °C overnight. After these procedures, the AMSC device was assembled successfully.

Supporting Information

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

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References

Figure 1. Schematic fabrication flow of the AMSC.

Figure 2. (a-b) SEM images of NCFs on CNTF at increasing magnifications. (c) Na-MnO_x nanosheets grown on NCFs. (d) Low-magnification TEM image of the Na-MnO_x nanosheets. (e) XPS spectra comparison of MnO_x and Na-MnO_x nanosheets. (f) EDX spectrum of Na-MnO_x nanosheets. (g) Low-magnification TEM image and corresponding EDS element mappings for Mn, O and Na of the Na-MnO_x nanosheet.

Figure 3. (a) CV curves of the Na-MnO_x@NCF/CNTF electrode at different operating voltages from 0.8 to 1.2 V at a constant scan rate of 25 mV/s. (b) CV curves of the Na-MnO_x@NCF/CNTF measured at different scan rates between 0 and 1.2 V. (c) GCD curves of the Na-MnO_x@NCF/CNTF electrode at different current densities. (d) Areal specific capacitance of the Na-MnO_x@NCF/CNTF electrode calculated from the GCD curves as a function of the current density. (e) CV curves of the VN@C NWAs/CNTF electrode measured at different scan rates between -1.2 and -0.2 V. (f) GCD curves of the VN@C NWAs/CNTF electrode at different current densities.

Figure 4. (a) Comparative CV curves obtained for the VN@C NWAs/CNTF and Na-MnO_x@NC/CNTF at a scan rate of 25 mV/s in a three-electrode system. (b) CV curves of as-assembled AMSCs measured at different operating voltages at a constant scan rate of 25 mV/s. (c) GCD curves of our AMSC device collected over different voltages from 1.2 to 2.4 V at a current density of 6 mA/cm². (d) Areal specific capacitance and energy density calculated from the GCD curves obtained at 6 mA/cm² as a function of the potential window.

Figure 5. (a) CV curves of the as-fabricated stretchable AMSC measured at different scan rates between 0 and 2.4 V. (b) GCD curves collected at different current densities between 0 and 2.4 V. (c) Areal specific capacitances calculated from the GCD curves as a function of the current density. (d) Areal energy and power densities of our AMSC compared with previously reported AMSCs. (e) One AMSC lights up an LED. (f) CV curves of the as-assembled AMSCs bent at various angles at a scan rate of 25 mV/s.